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News & Views

Scientific Value of Including an Atmospheric Sample as Part of Mars Sample Return (MSR)

Timothy D. Swindle,¹ Sushil Atreya,² Henner Busemann,³ Julia A. Cartwright,⁴ Paul Mahaffy,⁵ Bernard Marty,⁶ Andreas Pack,⁷ and Susanne P. Schwenzer⁸

¹University of Arizona, Lunar and Planetary Laboratory, Tucson, Arizona, USA.

²University of Michigan, Ann Arbor, Michigan, USA.

³ETH Zürich, Institute of Geochemistry and Petrology, Zürich, Switzerland.

⁴University of Alabama, Tuscaloosa, Alabama, USA.

⁵NASA Goddard Space Flight Center, Greenbelt, Maryland, USA.

⁶Université de Lorraine, CNRS, CRPG, Nancy, France.

⁷Universitat Göttingen, Göttingen, Germany.

⁸The Open University, Milton Keynes, UK.

Abstract

The Perseverance rover is meant to collect samples of the martian surface for eventual return to Earth. The headspace gas present over the solid samples within the sample tubes will be of significant scientific interest for what it reveals about the interactions of the solid samples with the trapped atmosphere and for what it will reveal about the martian atmosphere itself. However, establishing the composition of the martian atmosphere will require other dedicated samples. The headspace gas as the sole atmospheric sample is problematic for many reasons. The quantity of gas present within the sample tube volume is insufficient for many investigations, and there will be exchange between solid samples, headspace gas, and tube walls. Importantly, the sample tube materials and preparation were not designed for optimal Mars atmospheric gas collection and storage as they were not sent to Mars in a degassed evacuated state and have been exposed to both Earth's and Mars' atmospheres. Additionally, there is a risk of unconstrained seal leakage in transit back to Earth, which would allow fractionation of the sample (leak-out) and contamination (leak-in). The science return can be improved significantly (and, in some cases, dramatically) by adding one or more of several strategies listed here in increasing order of effectiveness and difficulty of implementation: (1) Having Perseverance collect a gas sample in an empty sample tube, (2) Collecting gas in a newly-designed, valved, sample-tube-sized vessel that is flown on either the Sample Fetch Rover (SFR) or the Sample Retrieval Lander (SRL), (3) Adding a larger (50-100 cc) dedicated gas sampling volume to the Orbiting Sample container (OS), (4) Adding a larger (50-100 cc) dedicated gas sampling volume to the OS that can be filled with compressed martian atmosphere.

1. Context and Conclusions

The Mars Sample Return (MSR) Program has as a current draft Level 1 Requirement:

“The MSR Campaign shall be capable of delivering to Earth at least one dedicated atmospheric gas sample of at least 1.9×10^{-5} mole of martian atmospheric gas molecules that is collected and stored in a clean and sealed volume.”

This team has been tasked with studying the scientific implications of returning, instead, one or more sample tubes from Perseverance, which would be sealed on Mars in the presence of martian atmosphere. This report was initially prepared for the MSR Standing Review Board.

We address two specific issues:

- (1) An individual sample tube on Perseverance would collect approximately 20% of the amount in the current draft Level 1 requirement, so we address the minimum amount of atmospheric sample needed to constrain high-priority scientific questions.
- (2) The sample tubes on Perseverance have been designed for collecting rocks, not atmosphere, so we analyze how that aspect might be different from a container designed for atmospheric sample return, and how that affects our ability to answer scientific questions.

We conclude that both the size and history of the sample tubes would cause a major loss in scientific value, compared to a sample collected in accordance with the draft Level 1 requirement. However, the return of a single sample tube sealed with only atmosphere inside would likely provide significant scientific value beyond that of the head space gas trapped in tubes containing rock samples, and we **strongly recommend** this as a minimum effort.

- The difference in the amount of sample returned between the two options is problematic. There are critical measurements (*e.g.*, the triple isotope system of oxygen in O_2 and the isotopes of N_2) for which the amount of gas in a sample tube collected at ambient pressure would be insufficient to answer the key scientific questions. In contrast, a 50 cc or 100 cc sample (the draft Level 1 requirement is approximately 60 cc) would be marginally sufficient. There are other critical measurements (isotopes of Ne, Xe, and C and triple oxygen isotopes of CO_2) for

which the amount in a sample tube would be marginally sufficient, but the number of aliquots analyzed might have to be fewer than the desired triplicate analysis. While technical advances in the next decade are likely to reduce the amount of sample needed for some analyses, it is not possible to reliably predict by how much. There are other key measurements, most notably the isotopic composition of CH₄ (methane), that are currently not achievable, even with the amount of gas specified in the draft Level 1 requirement; such measurements would require orders of magnitude technical improvements.

- There are critical measurements, including the relative elemental abundances of Kr and Xe and the isotopic composition of N₂, for which the history of manufacturing and exposure to atmosphere, water vapor, and dust the sample tubes have experienced, or will experience, would call into question measurements collected using the Perseverance sample tubes. The tubes that have been sent to Mars were not pre-treated in the same way that gas-collecting materials normally are in terrestrial situations (baked under high-vacuum conditions at >200°C for multiple days and then sealed until use). The materials used, notably the TiN coating of the inner walls, could potentially outgas or adsorb material before and/or after sampling, compromising the purity of the sample.
- For the head space in tubes that contain samples, the situation is even worse than collection in a dedicated sample tube because there will be a smaller amount of martian gas, and each of the samples themselves will have interacted with that gas, likely in various ways that will make the interpretation of any head space gas aliquot (or even the pooling of several gas samples) difficult.
- Calculations of the amount of leakage that will occur from a sealed sample tube have large uncertainties, though a best estimate based on limited data suggests that no more than a few percent is likely to be lost in most cases. That is more than would be desirable, and while that level of loss might be acceptable, if the leak rate is underestimated, it is possible that a sealed sample tube might not return any usable sample. Leakage in the other direction on Earth (*i.e.*, contamination by Earth atmosphere) could also be problematic. It will be difficult, if not impossible, to determine the leak rate for each tube, and the methods are yet to be developed.

- Although this team was tasked with determining how well the draft Level 1 Requirements would be addressed by sealing and returning one of the sample tubes already on Perseverance, and this report focuses on that, there are other options for returning samples of Mars atmosphere that would provide different levels of important scientific return.
- At one extreme, head space gas will be present in the tubes that contain the collected solid samples, and that head space gas will be derived largely from the martian atmosphere. However, for this scenario, all the problems listed above will be exacerbated compared to an empty sample tube, that is, the volume will be smaller, the samples themselves will provide multiple opportunities for exchange with the head space gas, and the process of putting the solid samples in the tubes will make leakage more likely.
 - If NASA and ESA decide to remove the draft Level 1 Requirement, we would *strongly* recommend that M2020 collects at least one gas sample using an empty sample tube. Such a collected sample would not only meet some of the draft Level 1 Requirement objectives but would also provide a critically important control (and thus standard) for gas geochemistry investigations involving sealed tubes that contain Mars samples and head space gas. However, research into the effects of the coatings of the tubes, the use of gold plating for the sealings, and their exposed environmental history (including the lack of baking and evacuation prior to sampling) would be needed to understand the details of the limitations of this technique.
- At the other end of the spectrum, a compressed sample of the same volume as that of the draft Level 1 Requirement would have significantly more scientific value than one that simply meets the draft Level 1 Requirement.
- An intermediate option is to collect gas in a newly designed sample-tube sized vessel that is valved with two valves and flown on either SFR or SRL. Such a vessel would not require additional space to return it compared to a typical sealed empty sample tube, although it would require development efforts. This strategy would alleviate concerns about the manufacturing and history of the collection container and provide a most robust mechanism for sealing (and testing the seal upon

return), and while it would not meet the draft Level 1 requirement for volume, the inevitable advances in detection technology that will occur before the return of the samples would mitigate this.

Findings

(1) When considering the head space gas in tubes with samples in them, we conclude that the relatively small volume, potential of seal leakage, and especially the likelihood of interaction of atmospheric gas with the sample and tube will make it difficult to answer any fundamental questions about the martian atmosphere.

(2) Although there are potential problems, most notably due to the possibility of interaction of martian atmospheric gas with sample tubes that were not manufactured, stored, or treated specifically for the task of atmospheric sampling, we conclude that a sealed sample tube containing only atmosphere (i.e., devoid of solid samples) recovered from Perseverance would likely provide significant fundamental science return about the martian atmosphere. Such a sample would also provide a much-needed baseline for interpreting the head space gas in tubes with solid samples. If taken, this option should be accompanied by a program to study the interaction of the tube materials with simulated martian atmosphere and their outgassing behavior.

(3) With consideration of upcoming Mars-targeted missions, we conclude that gas collected in a newly designed and purpose-built valved sample-tube sized vessel, which could be flown on either SFR or SRL, would be considered of higher priority than either the head space gas or a sealed M2020 sample tube. Conceptually, this vessel would require no more physical space to return than a sealed empty sample tube and alleviate concerns about the manufacturing and history of a non-purpose-built vessel, and the valving would provide a more robust mechanism for sealing the vessel and testing the seal upon return.

2. Structure of This Report

In Section 3, we discuss the species under consideration, calculate the amounts that would be acquired under various scenarios, and compare it to the amounts that would be needed for high-quality measurements using today's state-of-the-art techniques.

Section 4 discusses the effects of the container, including preparation, surface composition, storage history, and the possibility of leakage.

Section 5 is a summary of the basic points of the report.

Appendix 1 gives a history of previous groups' suggestions of requirements for a returned atmospheric sample.

Appendix 2 is a more detailed discussion of the scientific reasons for returning a sample of the martian atmosphere.

Appendix 3 is a detailed calculation of the effects of leak rates, based on measurements provided to us.

3. Species under Consideration and Amounts Needed

More details about the scientific rationale for measuring each of the species listed in Table 1 are given in Appendix 2, but the basic reasons driving the desire to measure each of these is as follows. The noble gases (He, Ne, Ar, Kr, Xe) are valuable for tracing the history of the atmosphere, including the original source of the atmosphere, additions to the atmosphere through martian mantle outgassing, and major processes such as past, catastrophic, and ongoing atmospheric loss. The triple oxygen isotopes in CO₂, O₂, CO, and H₂O are necessary to understand the triple oxygen isotope variations in secondary minerals within rock samples and thus provide valuable information about interactions between the atmosphere and rocks (and water). The isotopes of nitrogen are heavily fractionated in the martian atmosphere; detailed measurements of the isotopic composition, coupled with measurements in rock samples, can provide information about atmospheric loss, as well as outgassing from the interior. In many cases, these measurements are complementary. As a known marker for biological activity on Earth, methane (CH₄) in the martian atmosphere is of considerable interest. The amounts measured by Curiosity vary greatly (Webster *et al.*, 2015, 2018), and biological activity is one possible explanation for the levels detected. Though the amounts of martian atmosphere under consideration here are far too low to make the diagnostic measurements of isotopic ratios, as Jakosky *et al.* (2020) pointed out this could be accomplished with a compressed sample.

The highest priority measurements are as follows:

- **Triple oxygen isotopes in CO₂.** These provide a baseline for understanding the interaction of low-temperature minerals with the atmosphere, which constrains the amount of water present on Mars when those minerals formed. An even more complete picture of the hydrologic cycle on Mars can be obtained with measurements of O₂, CO, and H₂O in the atmosphere, but those species are progressively less abundant and, hence, harder to measure.
- **The elemental ratio of Kr to Xe.** Analyses of martian meteorites suggest Kr/Xe ratios that vary, and no precise *in situ* measurement has been performed. The observed variations are not understood and could have important implications for our understanding of the martian climate.
- **The abundance of cosmic ray produced isotopes of Ne, Kr, and Xe.** Curiosity measured an excess in ¹²⁴Xe and ¹²⁶Xe, compared to equivalent measurements in meteorites. If that excess is due to production by cosmic-ray interactions with rocks, followed by release into the atmosphere (a process that would have ramifications for martian atmospheric history), it should be accompanied by excesses in ⁷⁸Kr and ²¹Ne, isotopes which have not been measured *in situ*.
- **The isotopic composition of N₂.** This, in particular the relative abundances of N₂ isotopologues, will be diagnostic of processes that occur in the atmosphere. In addition, it could serve as an isotopic biomarker, indicative of processing by living organisms.

To evaluate what constitutes a necessary volume of atmospheric sample to achieve these priority measurements, we estimate in Table 1 the amounts of various species available in a sample tube (or a container of the same size as a sample tube), a 50 cc container, and a 100 cc container, each filled at ambient Mars atmospheric pressure. Note that a 50 cc container only provides approximately 85% of the draft Level 1 requirement so is used as a convenient size for purposes of example. Next, the abundance of the species in a single aliquot is calculated, assuming that, of the original sample, half is saved while the other half is divided into nine aliquots, to allow each of three laboratories to perform three

analyses targeting the species of interest. Finally, the amount of sample required for a high-quality measurement in a 2020 state-of-the-art laboratory is listed. This group was not tasked with determining the accuracy required to answer specific questions, so we have used “high-quality” to denote the amounts and conditions various specific laboratories consider adequate for publishable measurements. If the amount of gas available is less than what is considered necessary for high-quality measurements, it is, of course, possible to do fewer replicates (which reduces confidence in the accuracy of the measurements) or to make measurements with lower precision. In that case, those making measurements on the returned samples will have to make these difficult choices, but our purpose is to determine the amounts needed to make measurements at the current state-of-the-art.

In practice, some measurements require a separate aliquot, because measuring one species precludes measuring others—mass spectrometers consume the sample that they measure. In other cases, multiple species can be measured on a single aliquot in a mass spectrometer, or the measurement can be made by a technique that preserves the sample. Measurements with a tunable laser spectrometer (TLS), as would be preferred for CO₂, CO, and H₂O, do not consume sample, hence are a preferred method for initial atmosphere characterization. Mass spectrometric measurements of all the noble gases could be done on a single aliquot. Measurements of the isotopes of molecular oxygen (O₂) and nitrogen (N₂) could also be analyzed on a single aliquot, though not the same aliquot as the noble gases. Hence, to make all the measurements discussed above would require twice as many aliquots as any single measurement, which would mean that each aliquot available might be only half as large as stated in Table 1.

In terms of the amount of sample needed, it is clear that a single sample tube would provide sufficient sample to measure the noble gases and triple oxygen isotopes in CO₂, although CO₂ and the noble gas Xe are both within a factor of two of the amount available for a sample tube.

For CO and H₂O, the amounts collected for even a 100 cc container are far too small to acquire meaningful triple oxygen isotopic ratios. For O₂ and N₂, the amounts required are roughly three times the amount in a single aliquot of a 100 cc container. A precise

measurement could be made on fewer aliquots with present-day technology, but only by sacrificing a significant fraction of the sample, which would preclude measuring noble gas isotopes. We anticipate that with a decade of technical improvement, such measurements could be feasible. The situation is worse by nearly an order of magnitude for an empty sample tube (and worse still for those containing martian solids), which means that the instrument developmental efforts required to measure these would be even larger.

An alternate solution to filling a single tube and/or utilizing the head space gas of sample tubes would be to collect a 100 cc sample and compress it by a factor of 100, as proposed by Jakosky *et al.* (2020). Such a sample would make all the measurements discussed here possible, as well as enable measurement of the carbon isotopes in the enigmatic martian methane, a preferred solution from a scientific standpoint. The potential for contamination will also be less if a concentrated sample, containing far more moles, is analyzed. There are also numerous analytical advantages of collecting the present-day martian atmosphere sample in a container that is treated and sealed prior to launch rather than having been exposed sequentially to the terrestrial atmosphere, the vacuum of space, and the martian atmosphere.

Another option is to rely on analysis of martian atmospheric gases trapped in the head space of every sample tube filled with rock or regolith samples. There is likely to be valuable science that can be done with these, particularly with respect to improving our understanding of the interactions between the atmosphere and the returned rock or regolith samples. However, because the head space gas will have interacted with the geochemically different samples in many cases, it will be highly beneficial to know what the starting atmospheric composition would have been. The ability to extrapolate this information from the head space gas of sample tubes whose seals could leak at different times during MSR and with variable amounts of volume remains a key challenge for these types of atmospheric samples. Such head space gas samples likely will not enable us to answer key questions about the atmosphere. Additional limitations associated with the manufacturing and environmental history of the sample tubes, enumerated below, also apply. These complications are exacerbated by having a smaller volume of gas and more materials (the samples themselves) with which the gas can potentially interact.

4. Effects of Container Materials and History

In Section 3, we showed that collecting a sample of martian atmosphere in a sample tube would result in an amount that makes some measurements marginal or impossible with current technology, but is not dramatically different from the draft Level 1 requirement. However, the materials and history of the sample tubes are a larger consideration. Tube construction and exposure to varying conditions over time could alter many or all of the measurements of the atmospheric sample in ways that might not be possible to detect or address. These concerns are as follows:

The sample tubes were coated with titanium nitride, in a nitrogen atmosphere. Titanium nitride is far from an inert material at the atomic level (*e.g.*, Vojvodic *et al.*, 2006), so it is possible some martian (or terrestrial, as addressed below) species will be preferentially adsorbed or chemisorbed onto the sample tube walls. In addition, N₂ was used during the surface-coating process, and potential contaminants of this N₂ at trace element level (N₂ has 99.999% purity) can become trapped and then desorb later, producing contamination of N₂ and possibly other species in the gas. Note that N₂ is one of the listed priority measurements (Section 3). It may be possible to observe N₂ (at a low level) in the martian atmosphere, and terrestrial contamination from sample tube processing could place this measurement in jeopardy. Another of the key measurements noted in Section 3 is the ratio of the elemental abundances of the noble gases Kr and Xe (Kr/Xe). While a sample tube would collect enough sample volume to easily provide enough signal for an accurate measurement, Xe is known to readily adsorb onto surfaces, preferential to Kr, so any measurement of the Kr/Xe ratio would be suspect. Whether or not the best possible atmospheric sample to be returned is derived from the facilities available on Perseverance, all effort should be made to study the effects of the specific materials used for the sample tubes, by exposing analog tubes to a relevant series of conditions.

In addition, the sample tubes have been open since their manufacture and would not be sealed until some point on the surface of Mars. Therefore, sample tubes were not degassed at temperatures above 200°C under high vacuum pumping, as is required and done for lines and vessels used in noble gas and nitrogen laboratories. Baking under high

vacuum is required to remove adsorbed terrestrial atmosphere contaminants, which otherwise will contribute terrestrial contamination to martian gases. This also holds for parts of the seals, such as the Au plating that will be in contact with the sample. Plating can be the source of species, particularly Kr and Xe, which can be removed only by severe baking. This means that they will have been exposed to the terrestrial and martian atmospheres for months or years, while also spending many months in the vacuum of space, all the while undergoing thermal cycles in which gases might be trapped or outgas. This is potentially a problem for N₂, which will be difficult to measure anyway because of its low abundance, as well as for Kr and Xe, which readily adsorb onto surfaces. However, this would be an even worse problem if technical improvements make it possible to measure H₂O, since the water available for exchange might be either terrestrial or martian or a mixture of both. Typical preparation protocols for containers for use in high-precision gas measurements include high-temperature bakeout under vacuum followed by sealing until the desired gas is sampled, which is not possible for the sample tubes.

Finally, extensive tests of the seals on the sample tubes have led to the conclusion that there is a 95% chance that 80% or more of the tubes will leak He at a rate of 1×10^{-8} scc/s or less. In Appendix 3, we calculate the amount of leakage that could occur during a two-year period when exposed to the vacuum of space and find that 5% of the gas would be lost, assuming a He leak rate of 1×10^{-8} scc/s. This amount of loss would be a concern, but marginally acceptable. The tests performed to date suggest that it is likely that most tubes will have lower leakage rates, which would diminish the problem. However, we would not know the leak rate of a specific seal until the sample is returned to Earth, if then, and if only 80% of the sample tube seals are that tight, then 20% would be at higher levels. Furthermore, the likely event of dust from the martian environment settling onto the seals will increase the likelihood of leakage. So, it is also possible that virtually all the sample could be lost, rendering the effort useless. In addition, after arrival in the Earth's atmosphere, the pressure of Earth atmosphere will be two orders of magnitude higher than the content of the sample tube, with the partial pressure of nitrogen displaying an even larger difference, as nitrogen is a trace constituent in the martian atmosphere and the major constituent in Earth's atmosphere. Contamination, even with a small leak, could render some of the most important measurements impossible. For a dedicated container

with a valve, the leak rate of the actual container plus valve could be measured on Earth before it was sent to Mars. The dust risk increases with the duration of time the tubes are on Mars before being sealed, so if the atmospheric sample will be an empty tube on Mars 2020, earlier sampling would be preferable.

In summary, the draft Level 1 requirement for a “clean and sealed” volume appears critical for understanding any measurements of an atmospheric sample.

5. Summary

In terms of the size of the sample:

- The amount of Ar, Kr, Ne, and He in a sample tube would easily be sufficient to make replicate, high-quality isotopic measurements. For He, we do not know how much ^3He is in the martian atmosphere, but an amount below detection limits would set a scientifically important upper limit.
- The amount of CO_2 and Xe in a sample tube would be sufficient to make the desired number of replicate isotopic measurements, but the amount is within a factor or two of the minimum required for accurate measurements; larger samples, such as those required to meet the draft Level 1 requirement, would make it possible to make more measurements and/or measurements of larger aliquots of any given species, increasing the number of high-priority questions about the atmosphere that we will be able to answer.
- The amount of O_2 and N_2 in a sample tube would be insufficient to make any high-quality isotopic measurements. The amount in a 50 cc or 100 cc container would barely provide enough gas to make the minimum number of desired measurements, but could be sufficient with technical development.
- Without major technical advances, the amounts of CO , H_2O , and CH_4 of even a 100 cc container would be too small to make isotopic measurements that are precise enough to be meaningful.

In terms of the container:

- The sample tubes are coated with titanium nitride, a potentially active surface that could either adsorb sample gas or desorb contamination. The long-term net-effect of these two competing processes, particularly once the tubes are sealed on Mars, could be difficult to assess.
- The titanium nitride coating was applied in a nitrogen atmosphere, which could lead to outgassing of nitrogen and/or outgassing of trace gases within the coating atmosphere.
- The sealing mechanism contains Au-plated parts, which will have incorporated (terrestrial) gases present during the plating process. These gases can be a source of contamination if the equipment is not baked at a few hundred degrees centigrade under ultra-high vacuum conditions.
- The sample tubes have been open since their manufacture and will remain open until they are sealed on Mars, which will have provided ample opportunity for contamination through exposure to two different planetary atmospheres. There would be no opportunity to bake the tubes or the parts of the sealing mechanism that will be exposed to the sample before the sample is acquired.
- Adsorption and desorption onto the container surfaces will vary from species to species, and effects on elemental ratios of the species undergoing adsorption-desorption cycles is complex and might not be fully resolvable, calling any measurement, particularly an unexpectedly anomalous measurement, into question.
- The leak rate of the sample tubes, while low, is not constrained to be low enough for a single tube to prevent loss of a substantial amount of an atmospheric sample in space or contamination by terrestrial atmosphere after return.

Appendix 1: Prior Descriptions of the Requirement for a Dedicated Atmospheric Sample

A series of reports and studies of Mars Sample Return discussed the return of an atmospheric sample, leading to the current draft Level 1 Requirement of a dedicated atmospheric sample.

A Mars Exploration Program Analysis Group (MEPAG) Next Decade Science Analysis Group report (2008) said, “... it should be possible to recover the headspace gas . . . , although this gas will be significantly less useful for scientific purposes than a sample that has been isolated.” They did not use the word “dedicated.”

The report of the International Mars Architecture for Return of Samples Working Group (iMARS, 2008) did not use the term “dedicated,” but said (p. 20), “The gas sample should be isolated from the rock samples.” iMARS (2008) also wrote a set of draft requirements for an international MSR mission, and Requirement #9 is that “MSR will collect at least 1 gas sample of 10 cc at a pressure of 0.5 bar.” Note that this gas quantity is approximately one order of magnitude larger than the current draft Level 1 Requirement.

The term “Dedicated” was first introduced by the End-to-End International Science Analysis Group (McLennan *et al.*, 2012). Their Finding #18 was that “Gas geochemistry objectives would require the analysis of a dedicated martian atmosphere sample.”

All of this was input to the Planetary Science decadal survey, *Visions and Voyages*, which endorsed Mars Sample Return, including atmospheric sample return, as the top priority for flagship missions but was not specific about details of the atmospheric sample: “Refined criteria need to be developed for selecting sample suites for return to Earth, including sample suites for sensitive analysis of biomarkers (*e.g.*, CHNOPS elements); suites representing diverse sedimentary environments with possible rapid burial; suites showing chemical gradients formed through alteration, oxidation, neutralization, and precipitation; and those from aqueous alteration environments including hydrothermal suites that show potential for preserving biosignatures; igneous suites; regolith samples; and an atmospheric sample.”

Appendix 2: Scientific Questions Driving Atmospheric Sample Return

The scientific rationale for returning samples of martian atmosphere was addressed in the last Planetary Science decadal survey, *Vision and Voyages for Planetary Science in the Decade 2013–2022*, and more recently in a report by the International MSR Objectives and Samples Team (Beatty *et al.*, 2019) and a white paper to the upcoming Planetary Science decadal survey (Jakosky *et al.*, 2020).

Noble gas isotopic abundances

Noble gases (He, Ne, Ar, Kr, and Xe) are chemically unreactive, which makes them key tracers of planetary outgassing, atmospheric formation, and atmospheric evolution. In addition, they are relatively rare, so radioactive and other nuclear processes that produce a noble gas from a more common element can easily be traced.

Atmospheric isotopic compositions of all noble gases except He have been measured in martian meteorites (see review by Swindle, 2002), although corrections for the history of the meteorite often have to be made (*e.g.*, Cartwright *et al.*, 2014; Avice *et al.*, 2018). More recently, the SAM suite on Curiosity has measured the isotopic composition of Ar, Kr, and Xe, with results that generally, though not always, agree with those from meteorites (Conrad *et al.*, 2016). Of equal importance, due to the fact that Kr and Xe are being measured by using different volumes within SAM, and as a consequence of different measurement protocols, the elemental Kr to Xe ratio cannot be measured and was therefore not reported by Conrad *et al.* (2016). The lack of isotopic measurements leaves open tantalizing questions that might be answered with new measurements that could only be possible in the next two decades with returned samples.

Martian Xe is strongly fractionated isotopically relative to solar (nebula) Xe in a manner similar to terrestrial Xe. On Earth, this appears to be the result of a continuous process during the Hadean and Archean and is linked to H escape and therefore H₂O. Earth's atmosphere also contains recognizable contributions from the decay of ¹²⁹I and ²⁴⁴Pu. Mars' atmosphere contains a contribution from ¹²⁹I, but apparently lacks a contribution from Pu or U fission. Alternatively, the original noble gas reservoirs of the two planets might have been different. Higher precision measurements of the martian atmosphere are thus needed. In addition, the Curiosity measurement of martian Xe appears to show a puzzling contribution from cosmic-ray-spallation reactions within surface rocks producing ¹²⁴Xe and ¹²⁶Xe, a contribution that is not seen in the terrestrial atmosphere. For Kr, the major puzzle is that, while martian Ar and Xe appear to have been isotopically fractionated relative to solar compositions, martian Kr does not.

SAM was unable to measure Ne isotopes. In this case, there are contrasting interpretations of the meteorite gases at the tens-of-percent level for the ratio of the two

most abundant isotopes, ^{20}Ne and ^{22}Ne . This value, coupled with the known measurement of $^{38}\text{Ar}/^{36}\text{Ar}$, may make it possible to identify what processes are in action—thermal and/or non-thermal escape processes. In addition, the relative abundance of the least abundant isotope, ^{21}Ne , is even less well known from measurements made to date. Since ^{21}Ne can be produced both by nucleogenic processes in the martian mantle and by cosmic-ray spallation reactions in the very surface regolith layers, a precisely measured $^{21}\text{Ne}/^{22}\text{Ne}$ ratio could be coupled with models of outgassing of radioactive decay products in Ar and Xe and/or with models of cosmic-ray produced atmospheric excesses in Xe. Both relevant Ne isotope ratios ($^{20}\text{Ne}/^{22}\text{Ne}$, $^{21}\text{Ne}/^{22}\text{Ne}$) should be measurable with sufficient precision (<2%) in a container the size of a sample tube.

The abundance of He in the lower atmosphere is estimated to be (10 ± 6) ppmv, based on the latest analysis of the Extreme Ultraviolet Explorer and Phobos data (Krasnopolsky and Gladstone, 2005). This estimate is based on a detection in the upper atmosphere above the homopause, coupled with a radiative transfer model, to give the value in the lower atmosphere. The isotopic ratio $^3\text{He}/^4\text{He}$ has not been measured (^3He at the ppbv level or below is well below the detection limit by telescopic methods). With a returned sample, the abundance of ^4He can be measured with high precision, and even $^3\text{He}/^4\text{He}$ can be determined if the ratio is in the same range as that of the terrestrial atmosphere. Both these values will be invaluable for modeling degassing from the martian interior.

Heavy noble gas elemental abundances

The heavy noble gases Kr and Xe provide a fascinating conundrum: the martian meteorites do not show the same atmospheric Kr to Xe elemental ratio. Figure 1 highlights the different martian noble gas reservoirs and shows where the fractionated component lies: martian atmosphere as measured in the shergottite meteorites (MA; Bogard *et al.*, 2001) has a high $^{129}\text{Xe}/^{132}\text{Xe}$ isotopic ratio and a high $^{84}\text{Kr}/^{132}\text{Xe}$ elemental ratio of 20.5. Elemental and isotopic ratios for the martian interior (MI; Ott, 1988) are ~ 1 , whereas the “crush” component from Wiens (1988; component released by *in vacuo* crushing) has a low isotopic ratio, but a high elemental ratio. In this figure, AIR represents terrestrial air (Ozima and Podosek, 2002), EFA is elementally fractionated terrestrial air (Mohapatra *et al.*, 2009), and EFMA is an estimated hypothetical endmember of fractionated martian

atmosphere (Schwenzer and Ott, 2006). Elemental fractionation causes lowering of the $^{84}\text{Kr}/^{132}\text{Xe}$ ratio as observed in terrestrial water (blue triangle indicates an average ratio of ~ 15 for terrestrial waters; Ozima and Podosek, 2002) and in EFA. Most importantly for atmospheric sample return is to note that several martian meteorites (including the nakhlites and ALH 84001) have relatively high $^{129}\text{Xe}/^{132}\text{Xe}$ isotopic ratios, similar to the martian atmosphere, but much lower Kr/Xe elemental ratios than the shergottites. The shergottite Kr/Xe ratio is in better agreement with the measurements reported by the Viking landers, although the uncertainties of those measurements permit either that or the nakhlite/ALH84001 value. Returning a sample at a different time in the martian year compared to the measurements from Viking, or better even, two samples taken a few months apart, could answer two important questions: 1) What is the current Kr/Xe elemental ratio; and 2) How does this ratio change over time? Measuring the Kr/Xe ratio is of fundamental importance for understanding the signatures recorded in the martian meteorites and in allowing the full utilization of the knowledge that is already in-hand and constantly being delivered by new meteorites and further investigations of the martian meteorite suite. Without a returned sample, the martian meteorites and the Viking measurements remain our only data source with which to work, as the MSL SAM instrument is not able to measure the Kr/Xe elemental ratio. This measurement would also complement possible Kr/Xe ratio measurements in alteration materials in the returned samples, as fractionation occurs.

The origin of the elementally fractionated martian atmosphere in the nakhlite meteorites remains unclear, even though, by now, it has been investigated for over three decades (Ott, 1988; Mathew *et al.*, 1998; Gilmour *et al.*, 1998; Ott *et al.*, 2018). The elementally fractionated noble gases could have entered the rocks *via* the magma, either as an internal (crustal?) component or *via* magmatic assimilation from aqueously altered crustal rock (Gilmour *et al.*, 1999, 2001; Mathew *et al.*, 2003; Mathew and Marti, 2005). Alternatively, the elementally fractionated noble gases could have entered the rock during the formation of their aqueously altered minerals. In this case, elemental fractionation arose either as the atmosphere dissolved in the altering water or as alteration minerals formed in the rock (Drake *et al.*, 1994; Mohapatra *et al.*, 2009; Ott, 1988; Schwenzer and Ott, 2006; Ott, 2008; Schwenzer *et al.*, 2009; Swindle *et al.*, 2000; Cartwright *et al.*, 2013).

It is also possible that the Kr/Xe ratio changes with season or with climate. The abundance of argon in the martian atmosphere is known to vary seasonally (Trainer *et al.*, 2019), and Kr and Xe are more readily adsorbed than Ar. Even larger variations might occur if hydrate clathrates form (which has been proposed for Mars), since Xe could be preferentially incorporated (*e.g.*, Musselwhite and Lunine, 1995; Musselwhite and Swindle, 2001; Thomas *et al.*, 2007; Mousis *et al.*, 2009; Swindle *et al.*, 2009).

Oxygen isotopes in CO₂, O₂, CO, and H₂O

The $\Delta^{17}\text{O}$ of igneous silicate rocks from Mars is 0.3‰ (Franchi *et al.*, 1999). It has been observed that carbonates (Farquhar *et al.*, 1998; Farquhar and Thiemens, 2000), sulfates (Farquhar and Thiemens, 2000), and water (Karlsson *et al.*, 1992; Agee *et al.*, 2013) extracted from martian meteorites are not in equilibrium with the silicates and have (mostly positive) isotope anomalies. The origin of the anomalies, likely due to some atmosphere-mineral interaction(s), is not clear. Measurements of the isotope composition of martian atmospheric oxygen-bearing compounds are essential for understanding the mineral isotope compositions, the volatile evolution of Mars, and the atmosphere-rock interaction.

The martian atmosphere is very different from Earth's atmosphere as it is dominated by CO₂, has only a pressure of ~650 Pa, has undergone considerable escape to space, and is optically thin for UV light. The low density and absence of biologic O₂ allows UV radiation to penetrate through the atmosphere down to ground level. Photolysis of CO₂ to CO and O₂ can result in large 100‰ anomalies in $\Delta^{17}\text{O}$ in the reaction products (CO₂ photolysis at 184.9 nm; experiments by Bhattacharya *et al.*, 2000). A large positive anomaly in photolysis products would leave behind CO₂ with a small negative anomaly. Hence, the situation on Mars would be the opposite of that on Earth, where formation of O₃ with $\Delta^{17}\text{O} \gg 0$ (Thiemens and Heidenreich III, 1983; Heidenreich III and Thiemens, 1983) leaves behind a negative anomaly in O₂ (*e.g.*, Luz *et al.*, 1999; Pack *et al.*, 2017) because the source of O₂ (photosynthesis) has no anomaly. Because the ratio of CO₂/O₂ in the martian atmosphere is about 550 and a ^{17}O anomaly of O₂ of 100‰, the $\Delta^{17}\text{O}$ of atmospheric CO₂ would be about -0.182‰ (relative to the atmosphere's bulk composition of $\Delta^{17}\text{O} = 0\%$ relative to the Mars fractionation line). This is resolvable using tunable laser absorption

spectroscopy (TLS). Adding CO with $\Delta^{17}\text{O} \gg 0$ would result in a slightly lower anomaly of the CO_2 .

The triple oxygen isotope composition of atmospheric CO_2 , O_2 , H_2O , and CO would provide a unique picture of martian atmospheric photochemistry and allow an understanding of the anomalous signatures in martian minerals and water. If the anomalies observed in low- T minerals in Mars rocks are, indeed, atmospheric signatures, one could use these anomalies to obtain information, for example, on the availability of water during mineral formation. To demonstrate that these minerals actually carry anomalies inherited from the atmosphere, it is necessary to measure the atmosphere. Alternative scenarios, such as influx of anomalous cometary water, have been suggested to explain the anomalous composition of martian meteorite components (Karlsson *et al.*, 1992).

If, however, atmospheric components with distinct isotope anomalies can be identified, the presence of variable anomalous oxygen isotope signatures in low- T minerals on Mars could provide direct information about the availability of water at the time and location of mineral formation.

Nitrogen isotopes in N_2

The nitrogen isotopic composition of the martian atmosphere shows strong enrichment in ^{15}N , $\delta^{15}\text{N} = 572 \pm 82\text{‰}$ as measured by Curiosity (Wong *et al.*, 2013), where $\delta^{15}\text{N}$ is the deviation in parts per mil (‰) from the terrestrial atmosphere's N isotope composition. The enrichment in ^{15}N is due to preferential atmospheric escape of ^{14}N , although the exact mechanism is not well known. Some models of sputtering and photochemical escape of nitrogen to space suggest that exchange with surface/interior reservoirs is needed to buffer the nitrogen against excessive fractionation due to escape (Jakosky *et al.*, 1994). Refining this value at the per mil precision level would provide a robust N isotope baseline for investigating Mars atmosphere-interior interactions, as recorded in martian samples.

The terrestrial atmosphere shows a 19‰ excess of $^{15}\text{N}^{15}\text{N}$ (expressed as Δ_{30}) in air relative to a random distribution of nitrogen isotopes, attributed to gas-phase chemistry in

the thermosphere (Yeung *et al.*, 2017). This isotope disequilibrium is mediated by biological cycling and could be more pronounced on Mars in the absence of such cycling. Strong $\delta^{15}\text{N}$ enrichments observed in the atmosphere of Mars from isotope effects in photochemistry near the N_2 dissociation threshold suggest more extreme Δ_{30} values on Mars. Documenting the martian atmosphere's Δ_{30} would provide an independent means to understand processes of N_2 photodissociation and ionization. On Earth, nitrogen from the mantle and crust is isotopically equilibrated and does not present any excess of Δ_{30} . This difference with atmospheric N_2 provides a robust tracer of interactions between the surface and the interior of our planet (Labidi *et al.*, 2020). Assuming a similar situation on Mars, Δ_{30} measurements of martian rocks and minerals, as has been done for mantle-derived rocks on Earth, would make it possible to assess the extent of exchange between the martian crust, mantle, and atmosphere through time. Here, too, securing the exact nature of the martian signature is expected to help resolve the problems measurements of martian meteorites face due to the many other factors (from irradiation-induced isotopic changes during prolonged space travel to contamination by terrestrial atmosphere) that contribute to those signatures and unlock the knowledge these materials hold about Mars' past (Murty and Mohapatra, 1997; Mohapatra *et al.*, 2009; Mohapatra and Murty, 2010).

Nitrogen is a critical component required by all life on Earth, and the availability of nitrogen in the modern ocean strongly controls biological productivity (*i.e.*, Canfield *et al.*, 2010). The ultimate source of all biological nitrogen on Earth is atmospheric N_2 , where dissolved $\text{N}_2(\text{aq})$ transferred from the gas phase may be biologically reduced to NH_4^+ in a process called nitrogen fixation (or diazotrophy). This marks the critical first step of the biological nitrogen cycle (Canfield *et al.*, 2010; Stüeken *et al.*, 2016). Reduced nitrogen in the form of NH_4^+ (or other species) may also become incorporated in the mineral lattice of clay minerals or other hydrous phases (*e.g.*, Ader *et al.*, 2016). Because the processes of gas exchange, biological nitrogen fixation, and uptake into clay minerals (and many others) are known to exhibit observable and quantifiable fractionation between ^{15}N and ^{14}N , the isotopic composition of mineral-bound nitrogen is a critical biosignature that has been intensively investigated in modern and ancient systems (Ader *et al.*, 2016; Canfield *et al.*, 2010; Stüeken *et al.*, 2016). For this reason, the isotopic composition of mineral-bound or organic matter-bound nitrogen has received increasing focus in the context of Mars (*e.g.*,

Stüeken *et al.*, 2020). However, this biosignature may be rendered useless in the absence of constraints on the nitrogen isotopic composition of atmospheric N₂.

Appendix 3: Leakage during Return

The following calculation is an attempt to address how much leakage might occur from a sample tube sealed on Mars and returned to Earth. Our information on the experiments on the seals comes from the M2020 Sample Tube Seal V&V Evidence Package.

Assuming molecular flow, the system should obey the Knudsen equation, which is

$$q = k (P_2 - P_1)$$

where q is the flow rate (leak rate), k includes various parameters relating to the size and shape of the leak, and P_1 and P_2 are the pressures outside and inside the volume. In our case, we are most worried about leaks to the vacuum of space, so P_1 is effectively zero, and the equation becomes

$$q = k P$$

But q is proportional to the derivative with time of the pressure, dP/dt , so we can rewrite as

$$dP/dt = -K P$$

where K is some new constant, and the negative sign indicates that the pressure is dropping with time.

$PV = nRT$, so P is proportional to n , the number of moles, and it should be the same constant of proportionality on both sides, so

$$(1) \quad dn/dt = -K n$$

This equation is the basic radioactive decay equation, which can be solved as

$$(2) \quad n(t) = n_0 \exp (-K t)$$

where n_0 is the initial abundance.

Now we need to find K and t . We are given a leak rate of 1×10^{-8} scc/s of He, but we do not know what pressure (hence number of atoms or moles) that corresponds to. Let us assume the test is done with 1 bar of He on one side of the seal and a vacuum on the other

(we will consider the implications of this below). In that case, the appropriate K for a sample tube (which is 13 cc), would be (substituting into eqn. 1)

$$-1 \times 10^{-8} \text{ scc/s} = -K (13 \text{ cc}), \text{ or}$$

$$K = 7.7 \times 10^{-10} \text{ s}^{-1}$$

We will assume that the time in vacuum (the time in orbit, plus the trip time to Earth) is 2 years, or $6.3 \times 10^7 \text{ s}$

So we substitute this value into eqn. 2 and get

$$n(2 \text{ year}) = n_0 \exp \left[- (7.7 \times 10^{-10} \text{ s}^{-1}) \times (6.3 \times 10^7 \text{ s}) \right] = n_0 \exp(-0.0485) = \mathbf{0.95} \, n_0$$

This would indicate that 5% of the original He sample would be lost. By itself, this number is troubling (we would much prefer retention of 99% or more of the sample), but the larger concern is that there are order of magnitude assumptions made in the calculation, so the actual number could be significantly different in either direction.

- In a series of tests with and without dust or abrasion, and with variable forces applied to the seal, it was determined that abrasion was more important than dust, unless there was enough material to seriously affect the geometry of the seal, a circumstance unlikely to occur for a blank tube (but possible for the tubes with rocks in them). Subsequent tests with various stresses, such as thermal and vibration, of seals made in conditions designed to replicate the conditions on Perseverance, have so far returned leak rates below $1 \times 10^{-10} \text{ scc/s}$.
- We do not know the applicable pressure for the leak rate test. Our understanding is that the tests were done in a standard manner, with instrumentation under vacuum on the inside of the tube, and He atmosphere (under a “hat”) on the outside. Since the gas leaking into the tube is likely to be close to atmospheric pressure, but is not pure He, the partial pressure of He is likely to be less than one atmosphere, so K is likely to be larger than in our calculations, and the amount of gas retained is likely correspondingly smaller.
- Our understanding is that tests were done only for gas leaking from the outside of the seal in, as opposed to the direction we have been considering. These are likely

to be similar, if not identical, but it is not guaranteed. We have not presented an equivalent calculation for the leakage into the container after return to Earth, but the pressure differential is two orders of magnitude more, so the leak will be that much faster, adding a complicating effect. Actually, the difference in partial pressure for nitrogen is even more of a concern, since N_2 is the dominant species in the terrestrial atmosphere but occurs at the percent level in the martian atmosphere, with a different isotopic composition. Although Knudsen flow may not be applicable in this case, the equivalent calculation shows that an exposure on the order of minutes in the terrestrial atmosphere, or in a nitrogen-filled storage container, could change the N isotopic composition by more than 1‰, the desired measurement uncertainty.

- If the leak rate really is 1×10^{-10} scc/s, then with all other parameters kept the same, this calculation would give a retention of 99.95%, which is not a problem. On the other hand, if the leak rate is, instead, two orders of magnitude higher, this calculation would give a retention of <1%, leading to gas amounts that would not be measurable in many cases and to isotopic and elemental ratios that are fractionated. However, we will not know what the actual leak rate is until after the samples are returned, if then. If a dedicated container with a valve were constructed, the leak rate of the actual container plus valve could be measured both beforehand and afterwards.

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The decision to implement Mars Sample Return will not be finalized until NASA's completion of the National Environmental Policy Act (NEPA) process. This document is being made available for information purposes only.

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No competing interests.

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Acronyms Used

AIR	Terrestrial Air
ALH84001	Allen Hills 84001 Martian Meteorite
CHNOPS	Carbon Nitrogen Oxygen Phosphorous Sulfur
EFA	Elementally Fractionated Terrestrial Air
EFMA	Endmember of Fractionated Martian Atmosphere
ESA	European Space Agency
iMars	International Mars Architecture of the Return of Samples
M2020	Mars 2020
MEPAG	Mars Exploration Program Analysis Group
MSR	Mars Sample Return
NASA	National Aeronautics and Space Administration
OS	Orbiting Sample Container
SAM	Sample Analysis at Mars
SFR	Sample Fetch Rover
SRL	Sample Retrieval Lander
TLS	Tunable Laser Spectrometer

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Table 1. Quantities of atmosphere per container, assuming a sampling atmospheric pressure of 7.36 mbar.

Pressure (mbar)	7.36	Sample tube	100cc bottle	50cc bottle	Sample tube	100cc bottle	50cc bottle	Amount	
	Fraction of atmosphere	12.55 cc moles	moles	moles	Aliquots*	Aliquots*	Aliquots*	required moles	Lab‡
Total		4.07E-06	3.24E-05	1.62E-05	2.26E-07	1.80E-06	9.00E-07		
CO ₂	0.951	3.87E-06	3.08E-05	1.54E-05	2.15E-07	1.71E-06	8.56E-07	1.40E-07	Sakai et al. (2017)
N ₂	0.0259	1.05E-07	8.40E-07	4.20E-07	5.85E-09	4.66E-08	2.33E-08	1.00E-07	E. Young, UCLA
Ar	0.0194	7.89E-08	6.29E-07	3.14E-07	4.38E-09	3.49E-08	1.75E-08	7.00E-10	B. Marty, CRPG
O ₂	0.00161	6.55E-09	5.22E-08	2.61E-08	3.64E-10	2.90E-09	1.45E-09	1.00E-08	Young et al. (1998)
CO	0.00058	2.36E-09	1.88E-08	9.40E-09	1.31E-10	1.04E-09	5.22E-10	1.40E-07	Pineda et al. (2019)
H ₂ O	0.0003	1.22E-09	9.72E-09	4.86E-09	6.78E-11	5.40E-10	2.70E-10	1.40E-07	Kerstel et al. (2002)
He	1.00E-05	4.07E-11	3.24E-10	1.62E-10	2.26E-12	1.80E-11	9.00E-12	3.50E-15	H. Busemann, ETHZ
Ne	2.50E-06	1.02E-11	8.10E-11	4.05E-11	5.65E-13	4.50E-12	2.25E-12	2.16E-16	H. Busemann, ETHZ
Kr	3.00E-07	1.22E-12	9.72E-12	4.86E-12	6.78E-14	5.40E-13	2.70E-13	1.56E-14	B. Marty, CRPG
Xe	8.00E-08	3.25E-13	2.59E-12	1.30E-12	1.81E-14	1.44E-13	7.20E-14	1.04E-14	B. Marty, CRPG
All values assume atmospheric pressure of 7.36 mbar; fractions from Trainer et al. (2019) for CO ₂ , N ₂ , Ar, O ₂ , CO;									
Krasnopolsky and Gladstone (2005) for He; Owen et al. (1977) for Ne, Kr, Xe, and H ₂ O									
*Assuming 50% of sample saved for posterity, amount of aliquot available for triplicate analyses by each of three laboratories									
‡Reference laboratories. Note that these are chosen to represent 2020 state-of-the-art laboratories, and do not imply that these will be the laboratories that will actually analyze the samples									

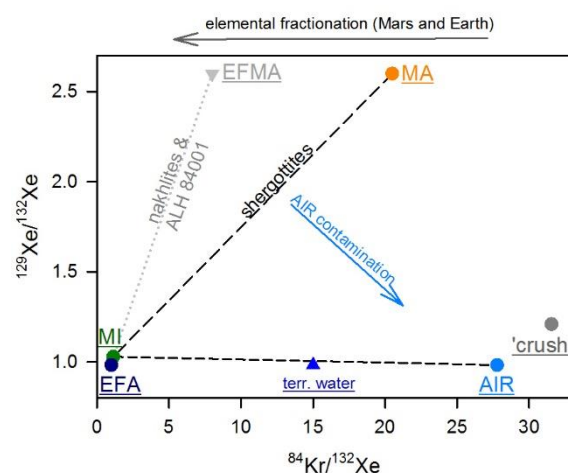


Figure 1. Endmembers as commonly used in martian meteorite heavy noble gas research. Endmembers are underlined, mixing and fractionation trends are indicated by arrows and lines.